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Excellent Leakage Current of Crystallized Silicon-Doped HfO_2 Films Down to Sub-nm EOT

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1. Introduction

It is widely believed that HfSiO is a promising high-κ material, but it has a lower permittivity (κ) than the pure HfO_2 due to the low permittivity (κ~3.9) of SiO_2. In the last SSDM, we have reported that a slight amount of Si doping into HfO_2 (SDH) enhances the film permittivity as shown in **Fig. 1** [1]. However, its origin has not been clearly explained. Furthermore, it is not quite sure that the gate leakage current of sub-nm thick EOT SDH is really advantageous than other HfO_2 – based high-κ films.

In this work, we have investigated the origin of the permittivity enhancement in detail. Furthermore, we have also investigated the scalability of SDH films down to sub-nm EOT region in terms of the dielectric constant, and the leakage current without nitrogen engineering.

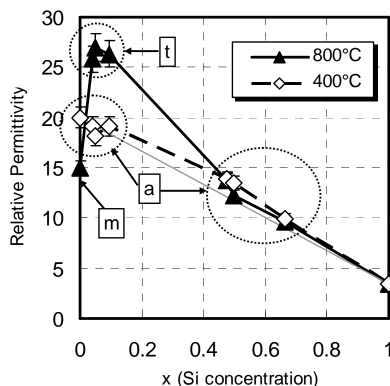

Fig. 1 Permittivity of SDH as functions of annealing temperature and Si concentration [1]. The character a, m and t denote the film structure as amorphous, monoclinic and tetragonal which were determined by XRD in this work.

2. Experimental

We fabricated MIM capacitors for electrical measurement using Pt film on Si. All the SDH films were deposited by co-sputtering method with HfO_2 and SiO_2 targets in Ar ambient. The samples were annealed at 400 and 800 ºC in N_2 + 0.1 % O_2 ambient for 30 seconds at the atmospheric pressure. For precise measurement, the SR in-plane XRD was employed. The film thickness was determined with grazing incidence X-ray reflectmetry and spectroscopic ellipsometry [2] and also checked with TEM images. The Si concentration was determined by X-ray photoelectron spectroscopy (XPS) and partly checked by secondary ion mass spectroscopy (SIMS).

3. Results and Discussion

As shown in Fig. 1, the permittivity of the 800 °C annealed samples shows a maximum value at x ~ 0.05, where the maximum permittivity of SDH (κ~27) is much higher than the permittivity of pure HfO_2 (κ~20: amorphous, κ~16:monoclinic). This result is not reasonable from the viewpoint of effective media model. In the last year SSDM, it was difficult to distinguish the crystal structure among the tetragonal, cubic and orthorhombic HfO_2, and that is still under debating [3]. In this work, we performed the high resolution SR in-plane XRD measurement for sample (x ~ 0.05) as shown in **Fig. 2**. The double peak near 35° indicates the possibility of the tetragonal or orthorhombic phase. Furthermore, it is suggested that the film was crystallized into mainly the tetragonal HfO_2 rather than into the orthorhombic phase with considering the crystal orientation and the peak intensity ratio. Although it is possible to consider that the film was crystallized into the mixture of some phases, it is concluded that the dominant phase of this film is the tetragonal HfO_2.

Here, we adopt the Clausius – Mossotti (CM) relation to analyze this permittivity enhancement [1]. In this equation, κ-value consists of α_m and V_m values, which are the molar polarizability and the molar volume, respectively. And κ-value enhancement comes from α_m increase or V_m decrease. In **Fig. 3**, α_m and V_m values of SDH film annealed at 800 °C are estimated by using XRD results and experimental κ-value. It is clearly observed that the tetragonally crystallized film has a much smaller V_m value than that of the monoclinic structure (x = 0). On the other hand, the α_m values are almost constant irrespective of x value. Hence, it is concluded that the κ enhancement is achieved by the V_m shrinkage associated with the crystallization rather than by the α_m enhancement.

Next, we discuss the intrinsic scalability of SDH films down to sub-nm EOT region. In MIS structure devices, the accurate EOT and J_g estimation are actually hard due to an

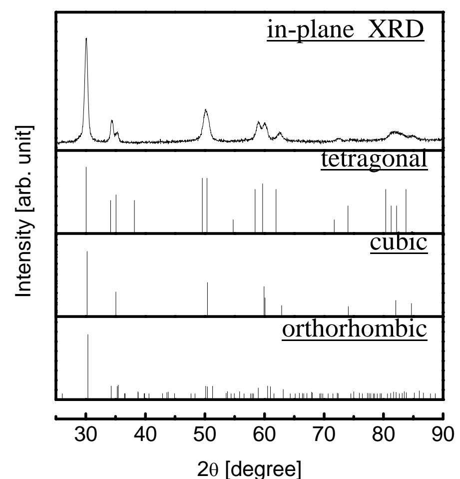

Fig. 2 In-plane SR-XRD measurement for crystallized SDH (x ~ 0.05) film. All the peaks can be consistently assigned to the tetragonal HfO_2 phase.

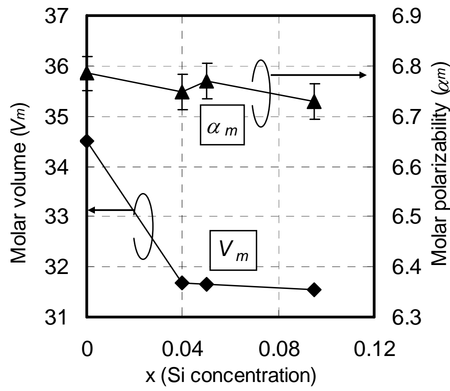

Fig. 3 Si concentration dependence of V_m and α_m values of SDH film. Pure HfO_2 (x = 0) is crystallized into the monoclinic phase.

existence of the interface layer. Then, MIM structure was used for SDH analysis in sub-nm EOT region. We measured the accurate capacitance by using impedance measurement, where log(-Im[Z]) – log(freq.) characteristics were measured because of large leakage current (**Fig. 4**). Very accurate capacitance values can be obtained for three element model [4]. By using the estimated capacitance values, the relationship between CET and T_{phys} is shown in **Fig. 5**. Even in MIM structure, a small amount of interface

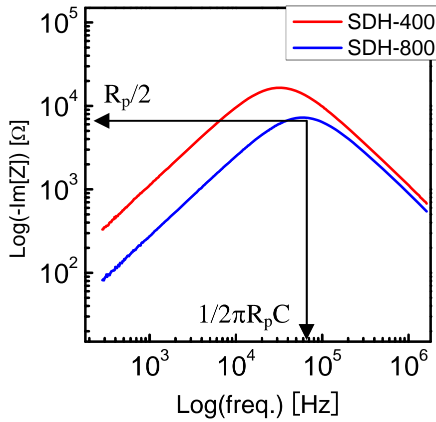

Fig. 4 Log (-Im[Z]) – log (freq.) plotsof 2nm SDH annealed at 400 and 800 °C. Rp and C means the parallel resistance and the parallel capacitance, respectively. Accurate capacitance can be evaluated from the peak height and the peak frequency.

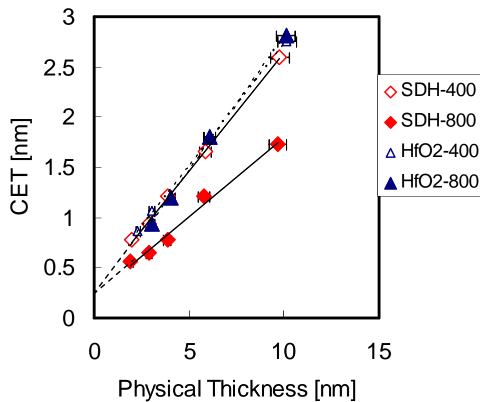

Fig. 5 Evaluated CET as function of Physical thickness. Despite the MIM structure, a small offset (~0.2 nm) is observed. The κ value of SDH annealed at 800 °C is about 25.

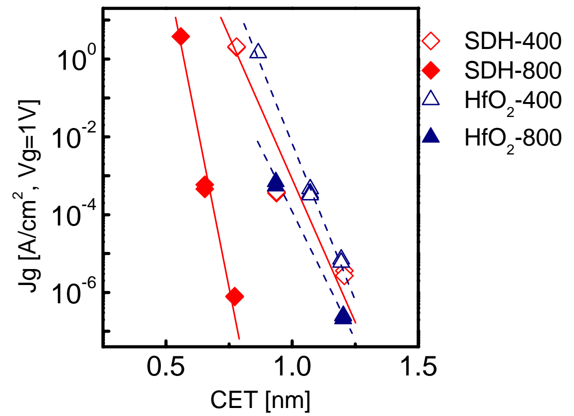

Fig. 6 J_g-CET for HfO_2 and SDH. The physical thickness of the films were 3nm or 4nm. SDH annealed at 800 °C reduces CET effectively without enhancing the leakage current.

layer by about 0.2 nm is observed, though the origin is not clear. From the slope of the results in Fig. 5, the dielectric constant of 800 °C annealed SDH in sub-nm EOT region is calculated to be about 25. It shows that SDH with T_{phys} = 2nm has almost the same κ-value with thick SDH.

Finally, gate leakage current (J_g) scalability is discussed. **Fig. 6** shows J_g at V_g=1V as a function of CET. Here, note that the offset of CET is about 0.2 nm as mentioned above, that is CET = EOT + 0.2 [nm]. It is clearly observed that J_g is not quite different among samples with a same physical thickness, while J_g in 800 °C annealed SDH is significantly reduced compared to the pure HfO_2. It strongly indicates that the Si doping and crystallization never affect the film leakage current in this thickness region. This fact means that the SDH with higher-κ is really promising material for scaling the gate dielectrics down to sub-nm EOT.

4. Conclusion

It was clarified with the SR in-plane XRD that the permittivity enhancement of SDH strongly related to the structural phase transformation into the tetragonal HfO_2. On the basis of the CM relation, it is concluded that the permittivity enhancement originates from the molar volume shrinkage rather than from the polarizability enhancement.

Furthermore, SDH annealed at 800 °C shows no increase of the leakage current in comparison with the pure HfO_2 or SDH annealed at 400 °C in spite of thinner EOT in sub-nm region, which means that SDH has a great advantage for the gate dielectric film scaling. It is suggested that SDH is really attractive material for the gate dielectric film scalable down to 0.5 nm. It was also confirmed that enhanced κ-value is maintained down to sub-nm EOT.

Acknowledgements

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